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Gentlemen:

I. INTRODUCTION

This program is concerned with the fabrication of metal carbide-graphite composites by hot pressing at temperatures up to 3200°C, and determination of physical and mechanical properties of these materials. Earlier studies on this project<sup>1,2</sup> have shown that dense, high-strength bodies could be produced by additions of as little as 6 vol% of the carbides on the Group IVA, VA or VIA metals. The strong bonding is obtained through solid and/or liquid (eutectic) diffusion in addition to plastic flow under hot pressing conditions. At a metal level of 10 vol% or higher, all of the carbide-graphite systems studied exhibit room-temperature flexural strengths of over 10,000 psi. These strength levels are retained or increase at 2000°C. Plastic behavior to varying extents are displayed for different compositions at 2500°C.

The greatest potential for high-temperature use has been shown by composites incorporating TaC or NbC. The purpose of this year's program is to fully characterize the properties of various compositions in these systems at temperatures up to 3000°C. Other

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systems which are of interest as potential high-temperature materials are ZrC-C and HfC-C. These compositions are only slightly less refractory than TaC-C or NbC-C and may offer certain advantages. Compositions incorporating ZrC have exhibited strength-to-weight ratios superior to those for TaC-C and NbC-C. HfC-C samples have shown an increase in strength at 2500°C over that at 2000°C; all of the other metal carbide-graphite systems which have been evaluated show maximum strength at about 2000°C. The molybdenum carbide-graphite system is also being investigated to determine the mechanism by which strong orientation of graphite is obtained through formation and migration of the Mo<sub>2</sub>C eutectic.

During the present period, experiments were conducted to more accurately establish hot pressing temperatures employing NbC-C eutectic formation as the indicator. Compositional studies have included systems incorporating zirconium carbide and hafnium carbide in addition to the TaC-C and NbC-C systems. Property determinations have been concerned with flexural and tensile strength, flexural creep at 2400°C and thermal expansion up to 2300°C.

## II. DISCUSSION

### A. Fabrication Studies

Temperature measurement during hot pressing is conducted both directly and indirectly. The direct method consists of optical monitoring with a Leeds and Northrup brightness pyrometer by sighting into the mold wall through an argon purged sight tube. Previous studies<sup>2</sup> have been made in which the temperature within the mold, i.e. where the sample would actually be located, was monitored concurrently with the standard mold wall measurement. It was determined that the two temperatures were virtually the same above 2800°C although a lag of about 50°C was observed at lower temperatures.

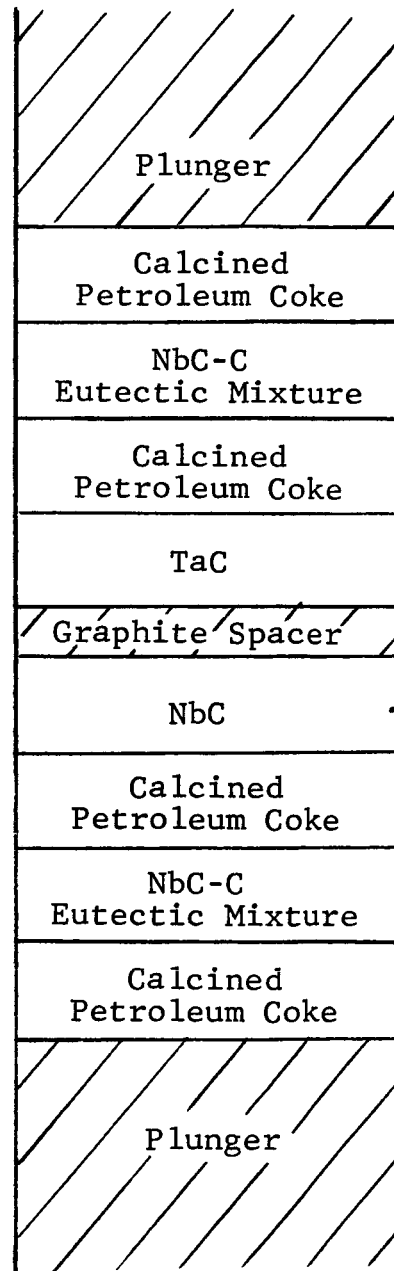
Temperature is also determined indirectly using time-temperature plots based on experimental data. The latter method becomes especially important at the higher temperatures where occasionally volatiles attenuate the transmittance of emitted radiation.

In some of our NbC-C pressings conducted at 3100-3200°C, loss of material and formation of the eutectic structure has suggested that the solidus had been exceeded. The NbC-C eutectic temperature has been variously reported at  $3305 \pm 15^\circ\text{C}^3$ ,  $3220 \pm 40^\circ\text{C}^4$ , and  $3220 \pm 50^\circ\text{C}^5$ , in recent literature. On the basis of our work, the latter temperatures would appear to be more realistic.

During this period, experiments were conducted to define more clearly temperatures attained during hot pressing. Eutectic mixtures of NbC-C were to be the "thermometer," i.e. formation of the eutectic structure would show if the solidus had been reached. As shown in Fig. 1, one eutectic layer was located toward the top of the mold and the other toward the bottom in an effort to determine possible temperature gradients. Also included were layers of TaC and NbC to determine possible diffusion of these materials into their carbonaceous surroundings. Layers of petroleum coke were used to separate the various layers so that the reactions in individual layers would be clearly defined.

The various materials were hot pressed at an indicated 3200°C and 3000 psi. Opening of the mold after the run revealed that most of the material had been lost through extrusion and reaction with the mold. The only layer which was clearly remaining was that of TaC. This suggested a very high mobility of NbC and/or NbC-C eutectic at these temperatures.

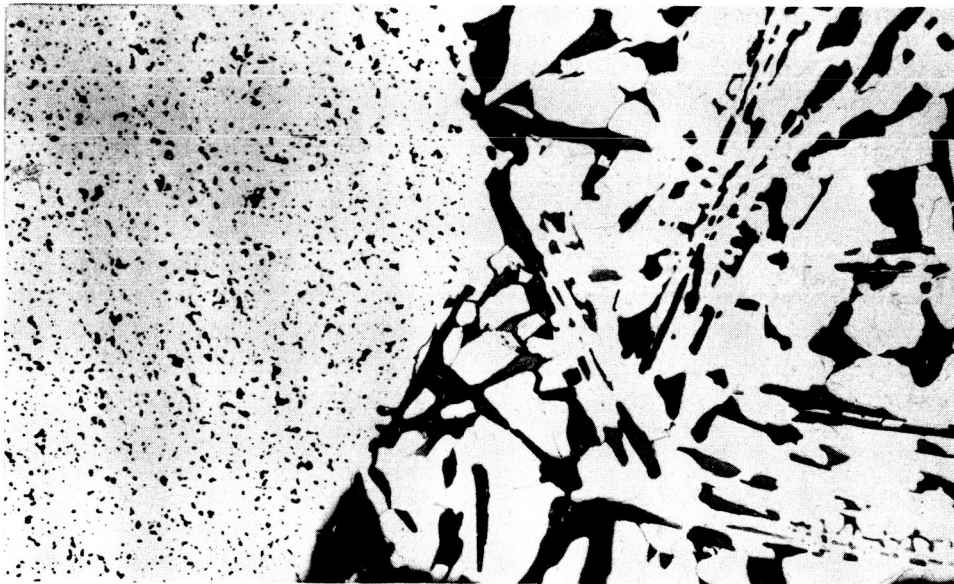
Photomicrographs of two areas are shown in Fig. 2. The eutectic structure (NbC-C) in Fig. 2a was material which had extruded from the NbC layer and had solidified on the side adjacent to the TaC on cooling. Apparently the solidus temperature had been exceeded during the run, as indicated by the eutectic.



Movement of NbC-C eutectic and subsequent crystallization (see Figure 2a)

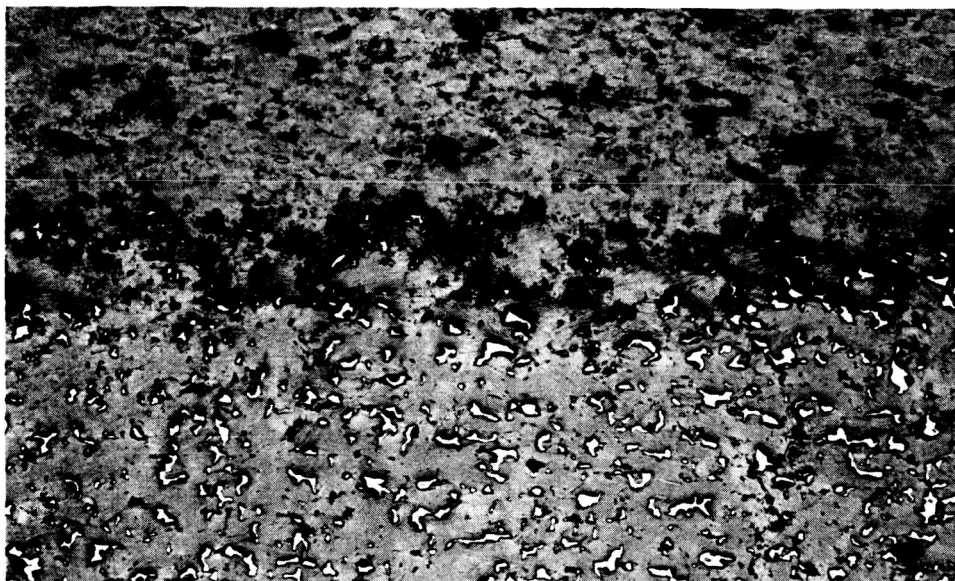
Note: Amounts of material used were designed to yield a finished height of  $\frac{1}{4}$ " for each layer

Fig. 1 - MATERIALS HOT PRESSED IN TEMPERATURE CALIBRATION STUDY (Test No. 1)



a) TaC

NbC-C



Calcined  
Petroleum  
Coke

NbC-C

b)

Fig. 2 - a) MICROSTRUCTURES OF TaC AND NbC-C EUTECTIC  
b) MICROSTRUCTURES OF ADJACENT COKE AND COKE-CARBIDE  
LAYERS SHOWING DIFFERENCES IN GRAPHITE STRUCTURE  
(125X)

The TaC phase appears rather porous; sectioning of samples from this layer and determination of densities revealed a range from 93.2 to 95.2% theoretical. Little if any solid solution between NbC and TaC occurred.

The layers depicted in Fig. 2B are for adjacent layers of NbC-C and calcined petroleum coke. Evidently much of the carbide had been extruded from the original eutectic (75 vol% NbC) mixture, leaving behind a structure corresponding to about 20 vol% carbide. The shape of the carbide particles suggests melting and recrystallization. This micrograph also shows very limited diffusion of carbide into the coke layer.

The beneficial effect of a liquid phase in producing dense graphite is also apparent in this micrograph (Fig. 2b). The carbon source in both layers was calcined petroleum coke. The layer which did not incorporate NbC was quite porous whereas the layer containing the carbide exhibits a dense graphite phase. Apparently movement of a liquid eutectic phase through the carbon and precipitation of graphite upon cooling results in the formation of a dense structure. A similar behavior has been shown<sup>2</sup> for graphite in which molybdenum carbide was the mobile liquid phase.

In view of the gross loss of material in the first experiment, a similar test was conducted at the same indicated temperature of 3200°C but at a reduced pressure of 500 psi. Some additions in materials were instituted in this pressing. As shown in Fig. 3, niobium metal foil and wire were imbedded into petroleum coke layers to act as diffusion couples. The purpose was twofold: one was to determine extent of carbide formation, and the second was to determine carbide diffusion into the graphite. Analysis for carbide diffusion into a graphite matrix by microprobe techniques has previously been conducted for composites incorporating NbC particles.<sup>1</sup> The evaluation was complicated by the fact that the x-rays penetrate to a depth of about 2-3 $\mu$ , thus revealing

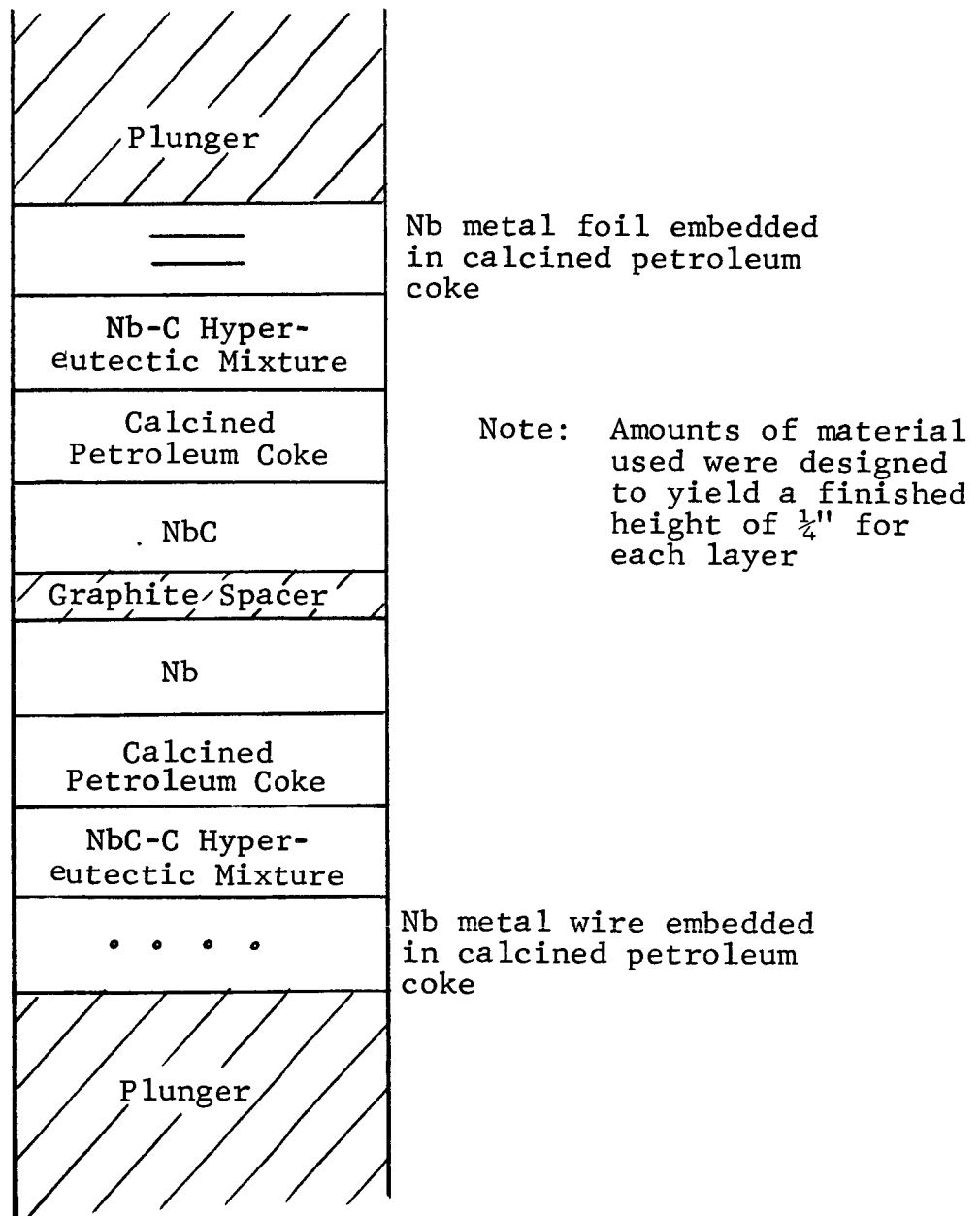


Fig. 3 - MATERIALS HOT PRESSED IN TEMPERATURE CALIBRATION STUDY  
(Test No. 2)

portions of carbide particles below the surface under examination. Therefore, it was difficult to determine if the carbide observed in the x-ray image was due to actual diffusion or merely to sub-surface carbide. The present experiment involving isolated wires of established diameter would permit microprobe analysis of the area surrounding the wire, eliminating sub-surface effects.

Examination of the mold interior after this pressing revealed that although material loss was again evident, much higher retention was realized with reduced pressure. The formation of a eutectic structure was evident in all of the layers as shown in the photomicrographs in Fig. 4. The Nb-C and NbC-C mixtures were designed as hypereutectics and both show excess graphite which had come out of solution. The carbide-carbon eutectic structure is also seen in the two layers which were originally pure metal and metal carbide containing no free carbon. During the pressing the metal formed the carbide and at the very high temperatures both carbide layers dissolved carbon from their environs in eutectic melting. Apparently diffusion of carbon into the carbide becomes quite rapid under these conditions. Graphite precipitates in these layers were observed at the boundaries with adjacent carbon layers.

A somewhat finer structure can be seen for the Nb-C and NbC layers which were in upper portions of the mold. This may be due to a slightly faster quench of the upper portions since heat loss on cooling would occur more rapidly toward the top, or open part of the hot pressing system.

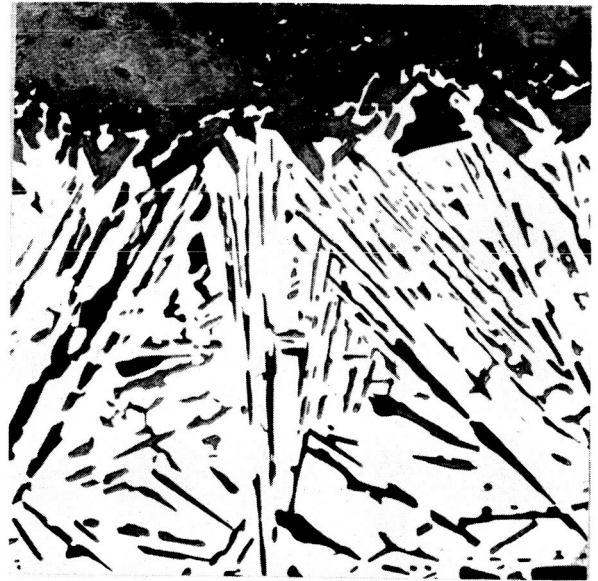
Macroscopic examination of the coke layer containing the metal foil showed little evidence of metal carbide phase. Microstructural study revealed areas containing small amounts of NbC particles, similar to that seen in Fig. 2B. Apparently much of the material had been lost through plastic flow.

On the other hand, the wire was retained in the coke matrix. As shown in Fig. 5, deformation of the wires due to the

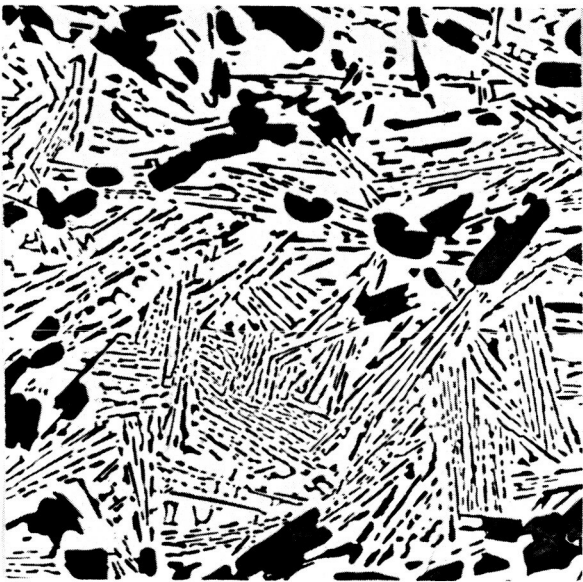




a) NbC Layer



b) Nb Layer



c) Nb-C Hypereutectic Layer



d) NbC-C Hypereutectic Layer

Fig. 4 - MICROSTRUCTURES OF NbC-C EUTECTICS  
FORMED IN HOT PRESSING (125X)



Fig. 5 - MICROSTRUCTURE SHOWING NbC-C EUTECTIC FORMATION  
OF Nb METAL WIRE IN GRAPHITE MATRIX (30X)

pressing direction is evident. Also in evidence is considerable material flow for one of the wires. Eutectic structure can be observed in both pieces showing that the metal had formed the carbide which in turn reacted with carbon to form the eutectic. The original diameter of the wire was 0.020 inches. A volume gain of about 70% can be expected in the carbide formation plus eutectic reaction. The structure on the left side of Fig. 5 conforms to such dimensional growth, whereas the larger growth for the structure on the right may be due to concentration of material flow in a particular area. Samples for microprobe analysis are now being prepared to determine carbide diffusion into the matrix.

These experiments show that NbC-C composites must be processed at temperatures below 3200°C in order to avoid liquid formation and subsequent loss of material. Additional pressings will be conducted at 3100° and 3000°C to accurately determine the maximum temperature which can be used without excessive loss of material.

Also shown by the present studies is the ability of niobium to readily form the carbide and subsequently dissolve carbon to form the eutectic. The completeness of the eutectic reaction is shown by the absence of any precipitate of primary carbide in the eutectic structure. Apparently carbon is continually dissolved until the mixture is of either eutectic or hypereutectic composition.

It is also apparent that the presence of a liquid NbC-C eutectic phase enhances densification of graphite. Part of this may be attributed to increased plastic flow. Another contributing factor is the high density and orientation of the graphite phase which precipitates from the eutectic. Full exploitation of such improvement in graphitization realized with the presence of a liquid carbide phase can lead to very high strength graphite matrix composites. Experiments are now being conducted in which

attempts are being made to contain and retain the liquid phase during hot pressing through the use of TaC as a liner material.

## B. Compositional Studies

During this period, compositions incorporating the carbides of zirconium and hafnium were fabricated for evaluation. A number of NbC-C and TaC-C billets were also processed for tension and compression tests. Compositions which were of particular significance are discussed in the following sections.

### 1. NbC-C Composites

Effect of Processing Temperatures - During the last report period, experiments had shown that lowering of the processing temperature from 3100° to 2850°C and soaking at this temperature for one hour yielded composites (C-65Nb) having good bonding (45 vol% NbC, 15,000 psi). Pressings were conducted under similar conditions but at a higher (4000 vs 3000 psi) pressure in an attempt to obtain even higher strength composites. These fabrications are designated C2-65Nb and C-66.4Nb; the data are presented in Tables I and II.

Flexural strength evaluations showed that the present composites were poorly bonded, exhibiting strengths of less than 10,000 psi. Densification was quite high, however, exceeding 96% for both billets. It appears unlikely that a pressure increase from 3000 to 4000 psi would yield a material having poorer bonding. It has been reported that intergranular diffusion leading to good bonding can be retarded by increasing stress in the hot pressing of  $\text{NiO}^6$ , but the pressure levels were 15,000 psi and higher. The present results suggest that the actual processing temperature was probably lower than the indicated 2850°C, limiting the degree of bonding which could occur. Difficulties in pyrometry were encountered in these runs due to an unusual amount of volatiles in the system.

Table I  
FABRICATION DATA FOR NbC-C AND TaC-C COMPOSITES

Compositional Designation	Form of Metal Addition	Pressing Conditions		As Mixed	
		Temp., °C	Pressure, psi	Wt% MC	Vol% MC
C-65Nb	NbC	2850(a)	3000	73.4	44.4
C2-65Nb	NbC	2850(a)	4000	73.4	44.4
C-66.4Nb	NbC	2850(a)	4000	75	46.5
C2-70Nb	NbC	2900(a)	3000	79.1	52.2
85 Ta	TaC	3200	3000	90.6	60.2
88 Ta	TaC	3200	3000	93.8	70.4

(a) One hour soak at temperature

Table II  
PROPERTIES DATA FOR NbC-C AND TaC-C COMPOSITES

Compositional Designation	<u>As Hot Pressed</u>		Density, g/cc	% Theoretical Density	Flexural Strength, psi	Grain Direction
	Wt% MC	Vol% MC				
C-65Nb	73.6	44.7	4.60	97.3	15,810 6,570	W/G A/G
C2-65Nb	73.7	44.8	4.57	96.4	9,830 4,790	W/G A/G
C-66.4Nb	75.2	46.8	4.71	97.1	9,500 6,100	W/G A/G
C2-70Nb	79.0	52.2	5.05	98.1	20,960 6,620	W/G A/G
85Ta	90.8	60.6	9.34	96.6	16,260 7,430	W/G A/G
85Ta	93.9	70.5	10.67	98.1	21,470 10,800	W/G A/G

On the other hand, high strengths were exhibited by sample C2-70Nb (Tables I and II) which was processed at 2900°C. These experiments indicate that in order for good bonding to occur, a minimal temperature must be attained. This temperature would appear to be in the range 2900°-2950°C. Diffusion mechanisms are apparently greatly accelerated at these temperatures leading to high strengths as well as high density.

## 2. TaC-C Composites

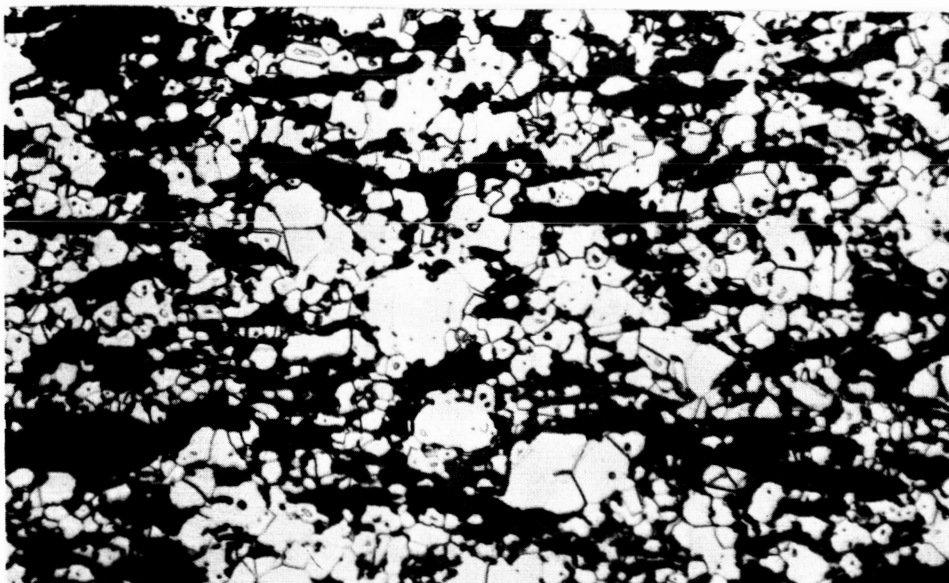
Two TaC-C composites having carbide contents of 61 and 71 vol% were fabricated for evaluation. These compositions lie between previously studied 50 and 80 vol% TaC composites, thus yielding additional data to establish compositional trends. These trends will be discussed in a later section dealing with mixing laws. Data for these composites appear in Tables I and II. Metal analysis revealed no loss of TaC, and both billets were easily removed from their respective molds. The fabrication temperature of 3200°C is well below the TaC-C eutectic of 3450°C, so there is no formation of a mobile reactive liquid phase as in the case of NbC-C.

Both 85Ta and 88Ta exhibited good densification and high strengths. Microstructures of these composites appear in Fig. 6, and little if any porosity could be discerned. Since the carbide is the dominant phase in these compositions, clustering of particles may be expected; this can be seen in both structures.

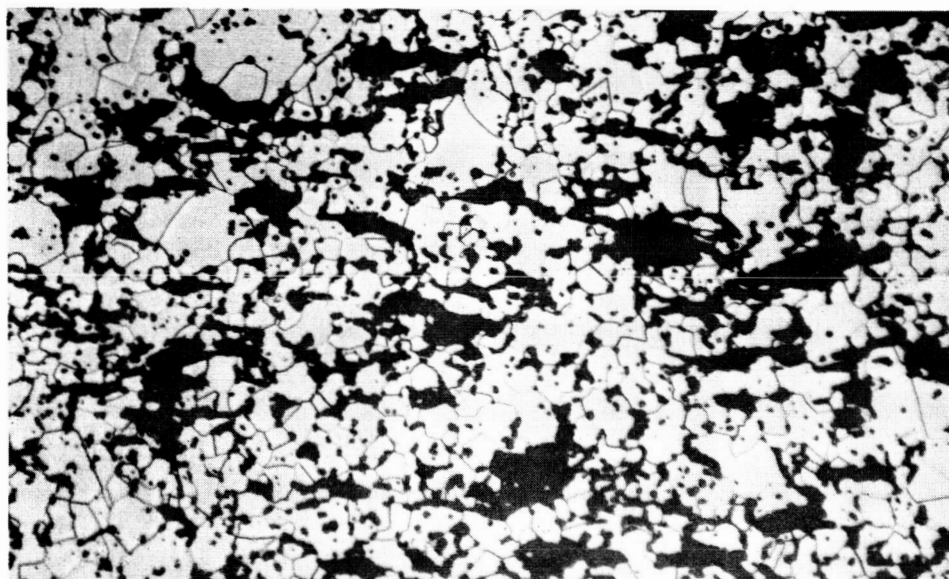
## 3. ZrC-C and HfC-C

The eutectic temperatures of ZrC-C and HfC-C systems are  $2890 \pm 50^\circ\text{C}$  and  $3150 \pm 50^\circ\text{C}$ .<sup>5</sup> These composites may be of interest if temperature requirements in any application are lowered. Compositional studies in these systems have been extended to obtain information on the effect of carbide content upon properties.

ZrC-C - Previous work<sup>2</sup> has shown that in hot pressing of ZrC-C composites containing 31 and 49 vol% ZrC at 3000°C, or about



85 Ta (61 Vol% TaC)



88 Ta (71 Vol% TaC)

Fig. 6 - MICROSTRUCTURES OF TaC-C COMPOSITES  
INCORPORATING 61 AND 71 VOL% TaC  
(320X)



100°C above the eutectic temperature, considerable metal losses were encountered. The finished composites contained 7.1 and 8.0 vol% ZrC, respectively, and both displayed flexural strengths of about 6000 psi.

In contrast, a molybdenum carbide-graphite composite hot pressed at 3000°C, or 400°C above the melting point of MoC showed a change in carbide content from a starting 21 vol% to a finished 13 vol%.<sup>2</sup> The flexural strength of this composite was very high (18,000 psi) despite the loss of metal carbide. A MoC-C of similar carbide content (21 vol%) was hot pressed at 3000°C for one hour. The carbide remaining was only 8 vol%; however, strength was still amazingly high (17,000 psi).

The amount of liquid formed in the 31 and 49 vol% ZrC-C mixtures would be about 40 and 60 vol% respectively of a carbide-carbon eutectic, or levels which are much higher than the 21 vol% liquid in the MoC-C system. In the present experiment, the starting ZrC content was reduced to 15% (or 19 vol% in terms of the ZrC-C eutectic). This composition corresponds closely to the MoC-C composites in liquid content which would be formed during hot pressing. As detailed in Tables III and IV, sample 30Zr-A was hot pressed at 3000°C. The carbide content of the finished billet was 7.0% or about one-half of the starting mixture. Little reaction with the mold was evident, and density determinations revealed variations of less than 2% through the billet. However, strengths were 9000 psi or only about a half of that shown by MoC-C samples. A similar difference in strength for MoC-C and ZrC-C systems have been reported by other investigators.<sup>7</sup> The reason for this disparity is not known at this time.

It would appear that lowering of the carbide content minimized the amount of material which could be lost through extrusion and reaction, thus preventing gross misalignment of plungers or excessive bridging between the sample and mold. Greater loss of material had previously lead to non-uniform and

Table III  
FABRICATION DATA FOR ZrC-C AND HfC-C COMPOSITES

Compositional Designation	Form of Metal Addition	Pressing Conditions		As Mixed	
		Temp., °C	Pressure psi	Wt% MC	Vol% MC
30Zr-A	ZrC	3000	3000	34.0	15.0
70Zr-A	ZrC	2800	3000	79.2	56.6
70Zr-B	ZrC	2700(a)	4000	79.2	56.6
80Zr-A	ZrC	2700(a)	4000	90.5	76.6
86Hf-A	HfC	2900	3000	91.8	66.6
86Hf-B	HfC	2900	3000	91.8	66.6

(a) One hour soak

Table IV

## FABRICATION DATA FOR ZrC-C AND HfC-C COMPOSITES

Compositional Designation	As Hot Pressed		Density g/cc	% Theoretical Density	Flexural Strength psi	Grain Direction
	Wt% MC	Vol% MC				
30 Zr-A	18.0	7.0	2.32	90.6	9,300 2,780	W/G A/G
70 Zr-A	78.0(a)	54.8	4.17	89.9		
	71.0(b)	45.6	3.31	78.1		
70 Zr-B	79.9	57.5	4.67	98.2	17,740 10,470	W/G A/G
80 Zr-A	91.0	77.7	5.51	97.7	20,030 11,980	W/G A/G
86 Hf-A	92.3	68.1	9.07	97.0	19,690	W/G
86 Hf-B	92.2	67.9	9.02	96.7	24,230	W/G
					8,860	A/G

(a) Lower portion of billet  
(b) Upper portion of billet

even prevention of pressing. This produced composites which were heterogeneous and weakened by voids.

It is interesting to note that the various ZrC-C composites processed at 3000°C all contained virtually the same amounts of carbide in the finished billets despite a wide range of starting content. It may be that the 7-8 vol% level is the amount of ZrC which would be retained in any ZrC-C under these conditions. A pressing will be conducted in which the starting content will be 7 vol% to determine if this is indeed a "tolerance" level.

Pressing of a 57 vol% ZrC composite at about 2800°C resulted in a poorly bonded, porous sample. Metal analysis showed that the loss of material was not exceedingly high, indicating that the eutectic temperature may have been just barely reached, and that the time of liquification was quite short.

Two composites processed at 2700°C or well below the eutectic were quite dense and well-bonded. As the data for 70Zr-B and 80Zr-A in Table IV show, densities were above 97% theoretical, and strengths of over 17,000 psi in the W/G direction and over 10,000 psi in the A/G direction were realized.

HfC-C - During this period, two billets of HfC-C were fabricated in which carbide is the dominant phase. The data as seen in Tables III and IV reveal high strengths for the 86 Hf samples. These materials will be subjected to high temperature tests to determine the effect of carbide content in the HfC-C system.

#### C. Properties Studies

In addition to the usual examination of density, microstructure and flexural strength, experiments were carried out at elevated temperatures to determine thermal expansion and flexural creep. Additional tensile tests have been conducted on TaC-C samples as well as those in the NbC-C system.

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## 1. Coefficient of Thermal Expansion (CTE)

Additional data has been gathered for thermal expansion behavior of NbC-C composites up to 2300°C. The values obtained for the compositions in the present studies fit the CTE vs carbide content curves reasonably well as shown in Fig. 7. An anomaly in earlier work had been that at 73 vol% NbC, the W/G expansion was slightly higher than that in the A/G or c-axis direction ( $7.49$  vs  $6.97 \times 10^6$  in/in/°C). The present CTE data for a higher carbide content material (86 vol% NbC) are  $7.44$  and  $8.11 \times 10^6$  in/in/°C in the W/G and A/G directions, respectively. Flexural tests have shown that even at these high carbide levels, anisotropy exists. Therefore, a higher A/G expansion would appear more logical. Values for the 73 vol% NbC may have been in error; additional work will be conducted with this composition.

In Fig. 8, CTE-carbide content relationships are presented for the TaC-C system for comparison. Both systems reveal a trend toward isotropic behavior with increasing carbide content. The strong anisotropy encountered with increasing amount of graphite is reflected in the exponential relationship suggested by data for graphite matrix materials.

## 2. High Temperature Flexural Creep

Earlier studies of high temperature creep had been conducted under compression at 2700°C/2000 psi/30 minutes.<sup>5</sup> Under these conditions, deformation was quite limited for all materials as shown in Fig. 9. This early data did indicate, however, that there appeared to be a direct relationship between creep and carbide content. This would appear logical in that the high temperature anelastic behavior of the carbide becomes more dominate in carbide matrix materials.

The present series of experiments were designed to give a clearer picture of this relationship. Tests were conducted in flexure at 2400°C/8000 psi/30 minutes, which was a far more severe

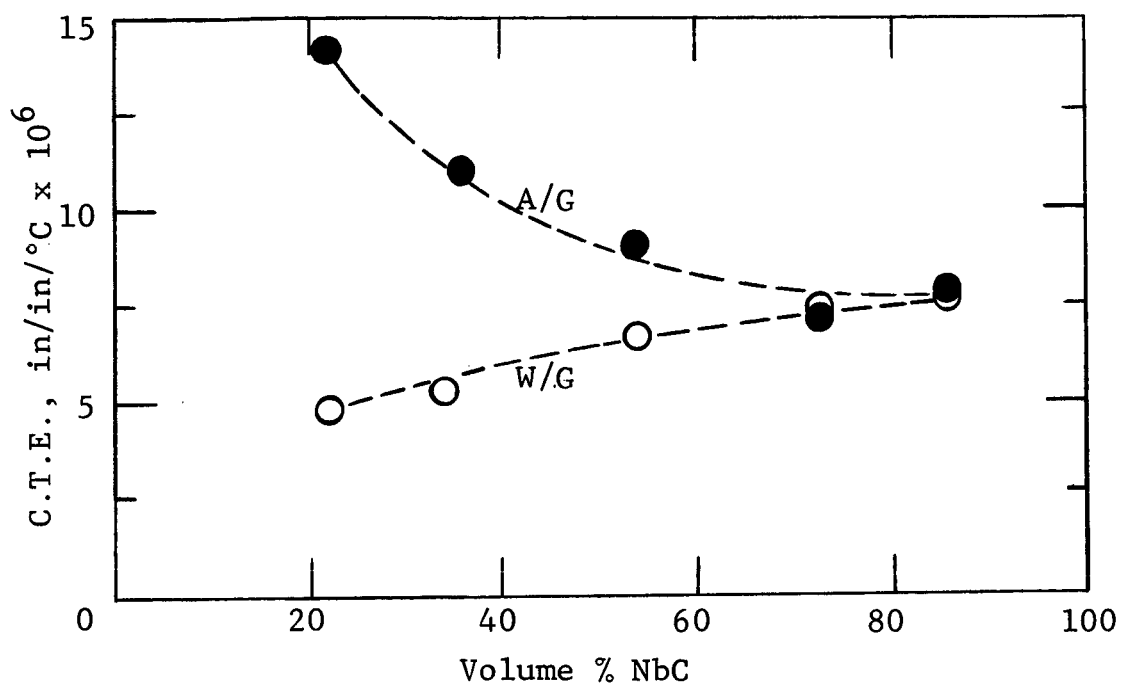


Fig. 7 - COEFFICIENT OF THERMAL EXPANSION VS. COMPOSITION FOR NbC-C COMPOSITES (RT - 2300°C)

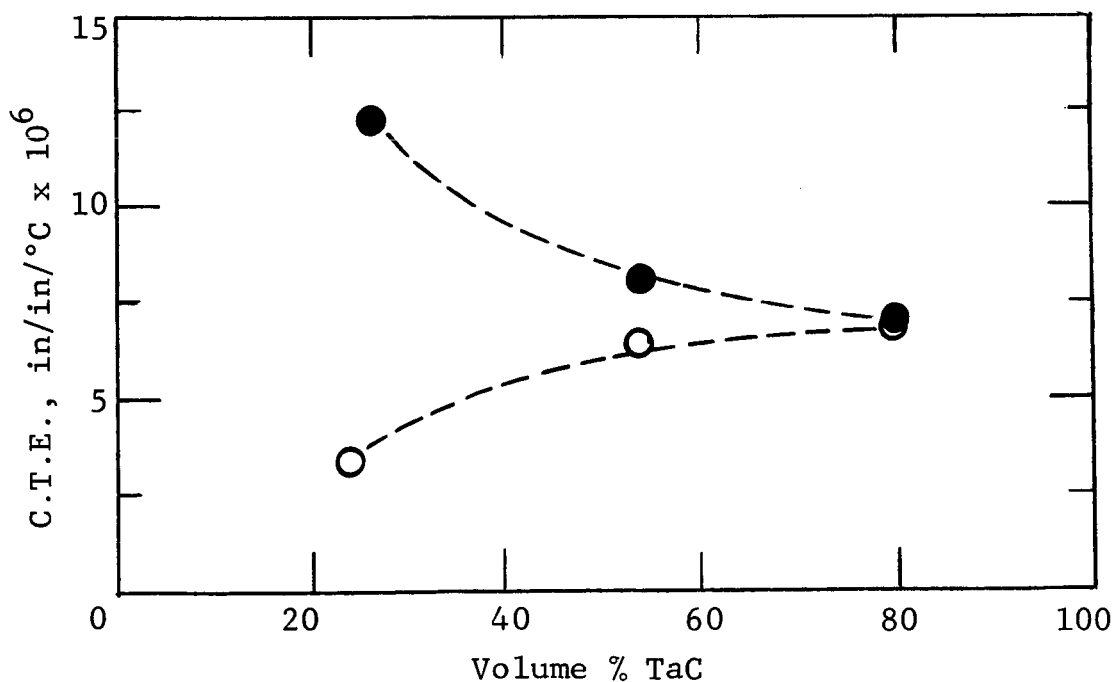


Fig. 8 - COEFFICIENT OF THERMAL EXPANSION VS. COMPOSITION FOR TaC-C COMPOSITES (RT - 2300°C)

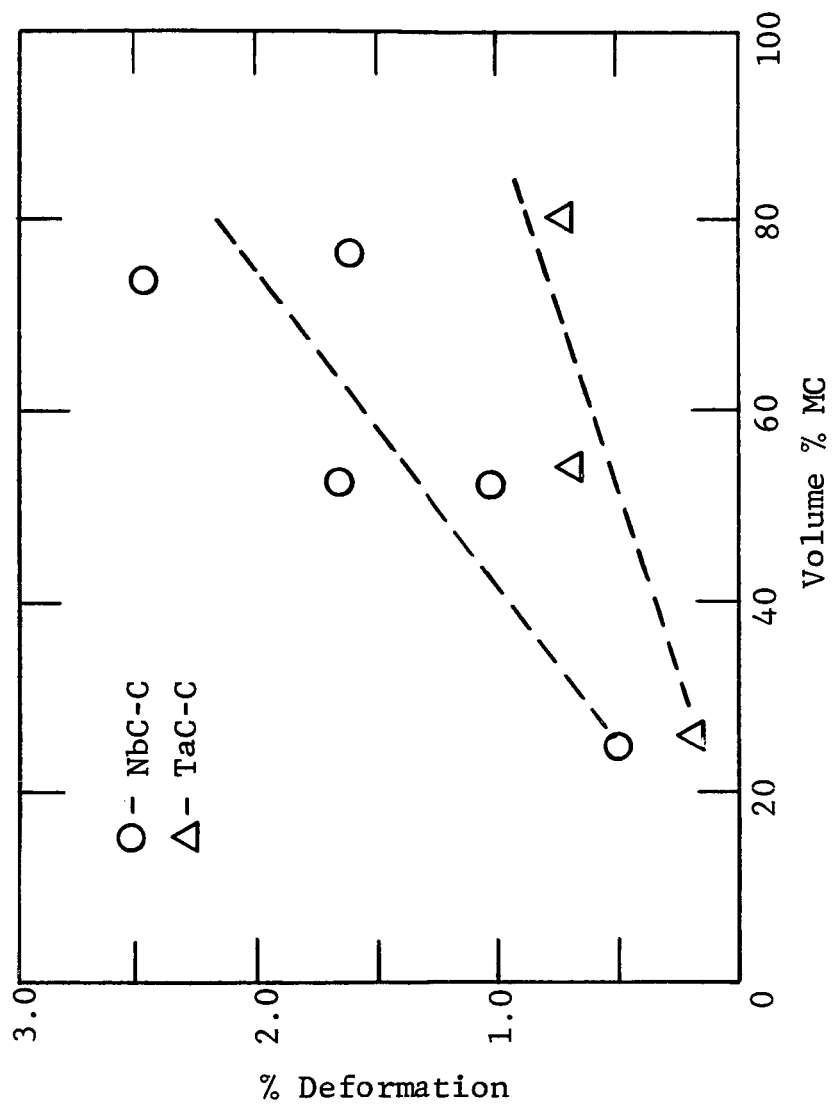


Fig. 9 - COMPRESSIVE DEFORMATION VS COMPOSITION  
FOR NbC-C AND TaC-C COMPOSITES  
(2700°C/2000 psi/30 min)

set of conditions and exaggerated differences in creep resistance due to carbide content. Materials are much more creep sensitive under the tensile forces set up in flexure than they are to purely compressive forces. Four point loading with a bottom span of  $2\frac{1}{4}$ " and a top span of  $\frac{3}{4}$ " was used. Deformation was monitored optically by sighting on the sample using Gaertner optical micrometers.

Plots of deformation at  $2400^{\circ}\text{C}$  under load and permanent deformation after load release appear in Fig. 10 for various compositions. The data suggests increasing susceptibility to creep with increasing carbide content. However, a reversal in this trend was observed for samples incorporating 86 vol% NbC. The density values show that this shift in the curve is probably not due to porosity, since the materials (52 and 74 vol% NbC) which had exhibited strongest deformation also had the highest densities. Although this reversal was observed, the curves show that graphite matrix materials, i.e., those containing 22 and 35 vol% NbC, displayed the smallest amounts of deformation among the compositions evaluated. Experiments will be continued to determine the validity of this preliminary data.

The permanent deformation curve shows that recovery after removal of load becomes smaller with increasing carbide content. The 22 vol% NbC composite exhibited a 50% recovery whereas the 86 vol% material displayed practically no recovery. Apparently much of the deformation observed for the higher carbide composites is plastic in nature. In graphite matrix materials elastic behavior is much more in evidence.

A TaC-C composite containing 81 vol% TaC was also included in this evaluation. The creep resistance of this material was extremely good and was far better than the best NbC-C material. Based on previous data, it appears likely that lower carbide content TaC-C composites will also perform as well.



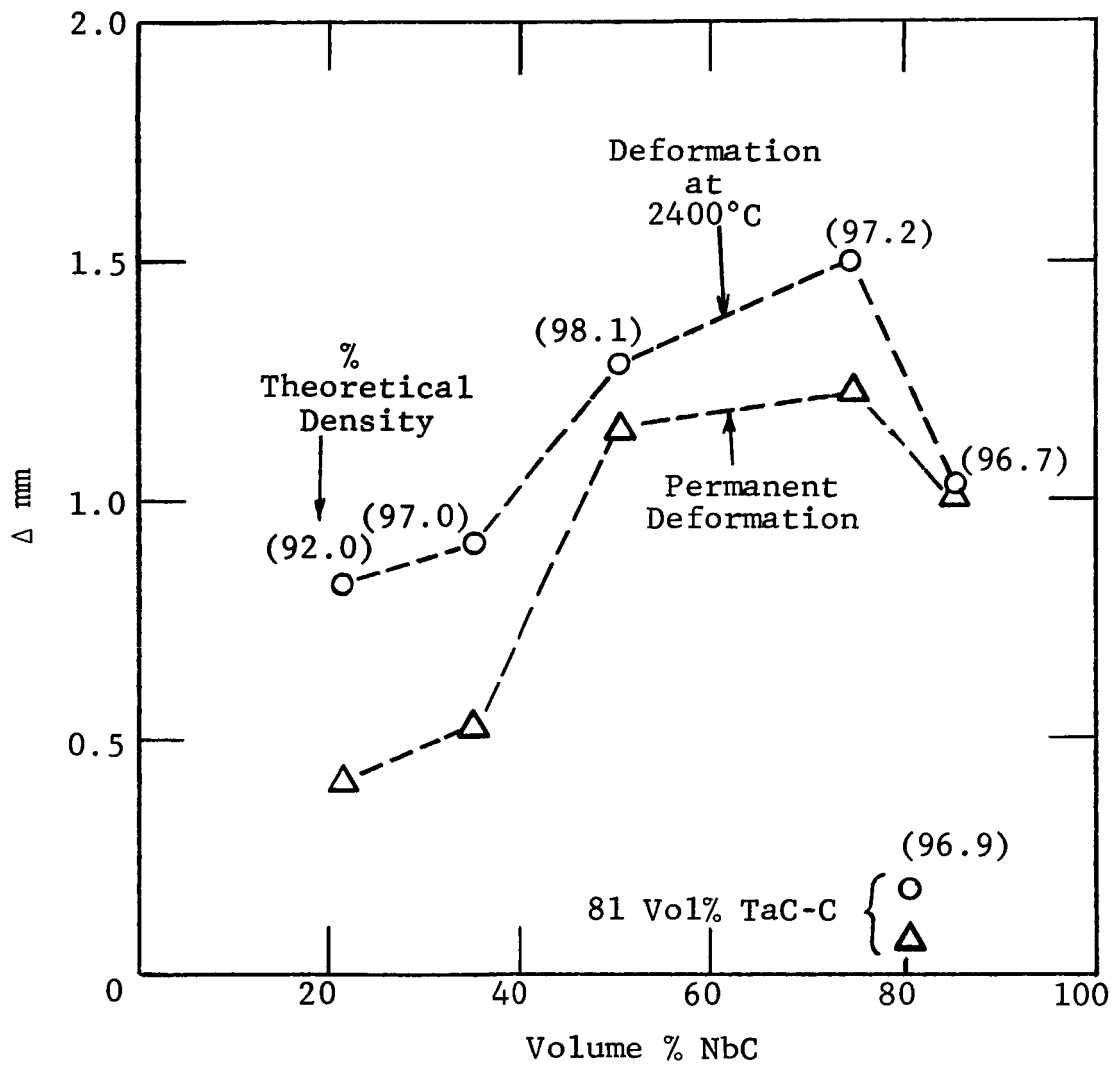


Fig. 10 - FLEXURAL CREEP BEHAVIOR OF NbC-C COMPOSITES  
(8000 psi/2400°C/30 min)

### 3. Tensile Strength Measurements

Room temperature tensile strength tests have been continued during this period. Pin-type tension specimens described in the last quarterly report were used. The data are as follows:

<u>Composition</u>	<u>Vol% MC</u>	<u>Tensile Strength, psi</u>
80Nb-E	73 (NbC)	18,610
84.1Nb-L	83 (NbC)	21,200
M90Ta-A	80 (TaC)	14,970
90Ta-B	80 (TaC)	19,550

Values are quite high for the various composites with the exception of M90Ta-A. This differed from 90Ta-B in that the carbide particle size was about  $3\mu$  for 90Ta-B and about  $10\mu$  for M90Ta-A. Thus, the lower strength may be due to the larger particle size in M90Ta-A. Samples are now being sectioned from the same billets for flexural tests so that a comparison of tensile and flexural strengths can be made for the same material.

High temperature tests are anticipated shortly. Modifications have been made on a Brew furnace-Riehle testing machine apparatus, and compressive tests will also be conducted in the near future.

### 4. Application of Mixing Laws

During the last report period, mixing laws were applied to our data in an attempt to gain a better analysis of behavior in our two phase systems. Theories of multiphase materials and laws of mixture have been proposed to establish upper and lower bounds for the effective elastic constants of heterophase materials.<sup>9</sup> These bounds are determined from acceptable displacement of stress fields within the multiphase material. In a two-phase system the upper bound can be interpreted as uniform strains on the phases and is represented as

$$E_s = E_1 V_1 + E_2 V_2 \quad (1)$$

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The lower bound is a uniform stress model in which the strain on the individual phases is different. The relationship here is

$$\frac{1}{E_s} = \frac{V_1}{E_1} + \frac{V_2}{E_2} \quad (2)$$

Models for these relationships appear in Fig. 11

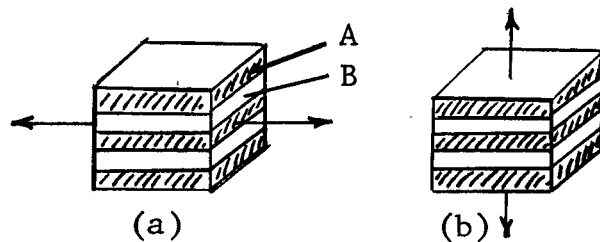


Fig. 11 - MODELS OF PARALLEL AND SERIES SYSTEMS  
(a) Parallel or Constant Strain Model of Two Phases A and B: (b) Series or Constant Stress Model of Two Phases A and B

The early analysis has shown that flexural strengths in the W/G direction followed a linear, or upper bound type of relationship with respect to carbide content. The work for this period has been to evaluate data in the A/G direction, and also to establish the behavior of pure NbC so that the strength vs carbide content plot might be extended.

Evaluation of Flexural Strength in A/G Direction - With the preparation and evaluation of additional composites, data in the A/G direction have been gathered and an analysis can now be made. Representative plots of flexural strength in both grain orientations as a fraction of NbC content appear in Fig. 12; similar plots for the TaC-C system are presented in Fig. 13.

A linear, or upper bound relationship is seen to exist in the W/G direction for both systems and the data for A/G strengths suggest exponential, or lower bound relationships. This may be explained by referring to the models in Fig. 11.

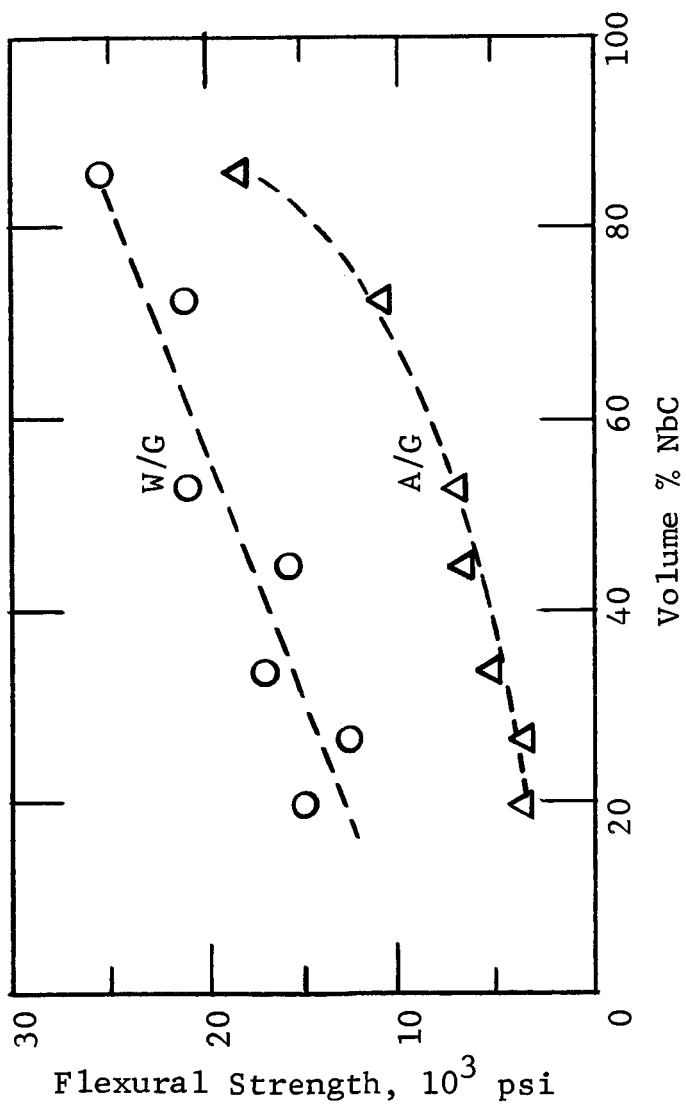


Fig. 12 - FLEXURAL STRENGTH VS. COMPOSITION  
FOR NbC-C COMPOSITES

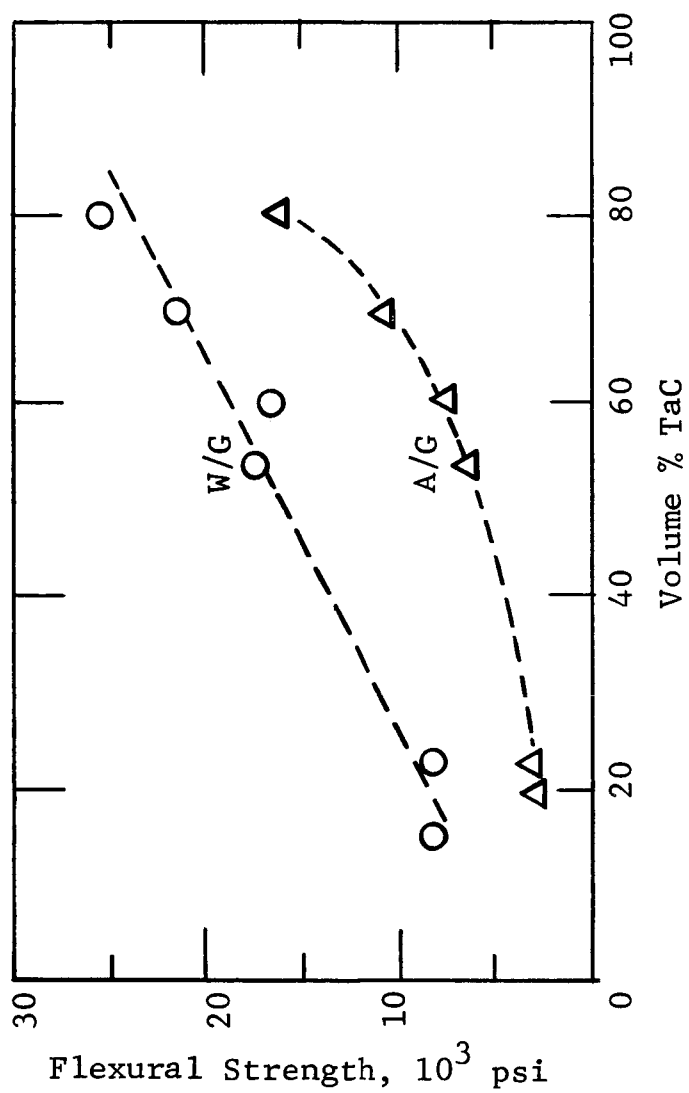


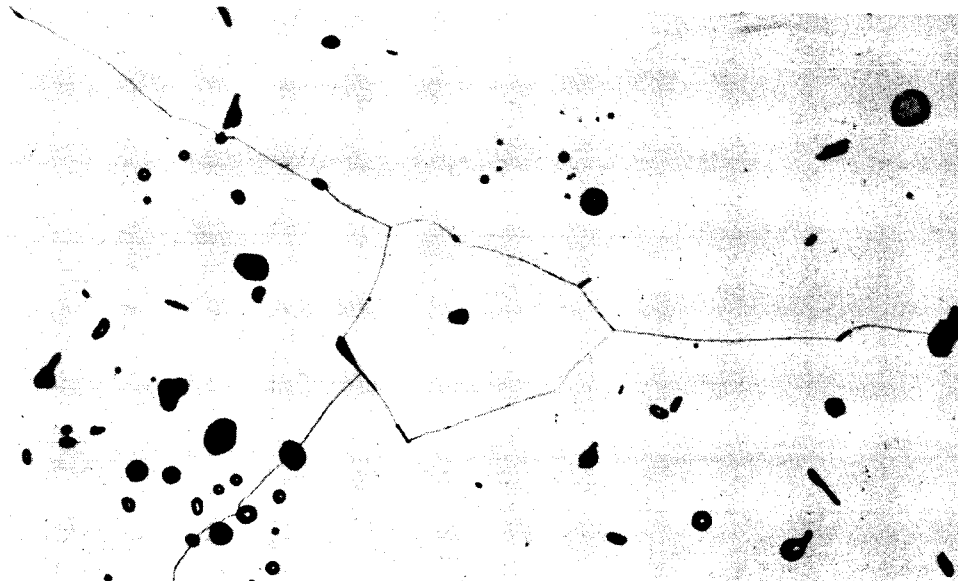
Fig. 13 - FLEXURAL STRENGTH VS COMPOSITION  
FOR TaC-C COMPOSITES

Flexural stresses set up in the W/G direction are analogous to the parallel model, i.e., A and B in Fig. 11a. can be considered as oriented carbide and graphite particles which are under constant strain. When composites are tested in the A/G direction, the stresses introduced in flexure are now perpendicular to the carbide and graphite "layers" and a series or constant stress model as depicted in Figure 11b applies.

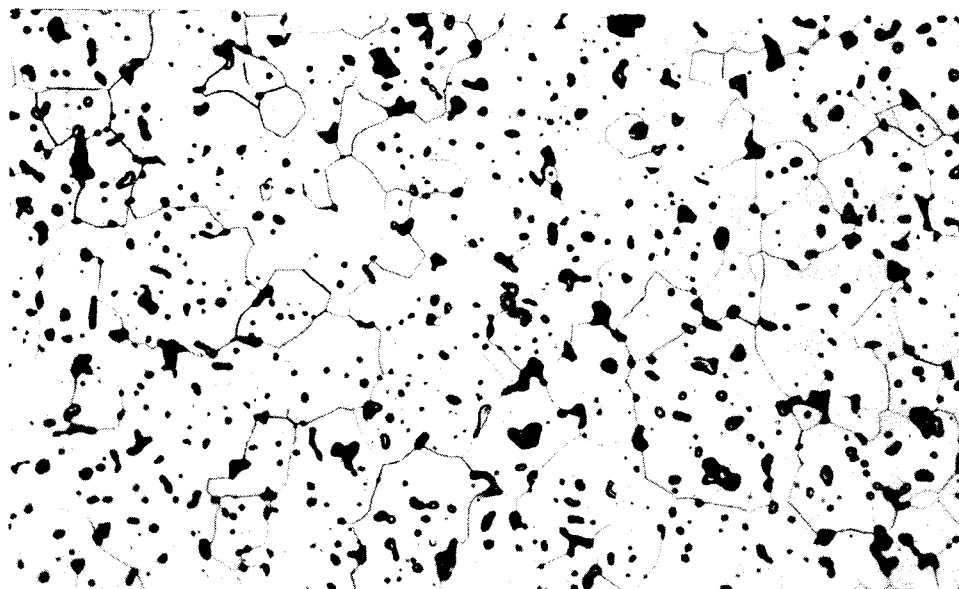
These data show that even at 50 vol% metal carbide, the anisotropy ratio in flexural strength is still greater than 2:1. It is only at the higher carbide contents of about 70 vol% that a greater trend toward isotropic behavior becomes apparent. Such anisotropy exists almost by definition for graphite matrix composites. When the volume percentage of carbide is raised to about 50, however, greater isotropy may be achieved by sintering of the carbide particles in the direction parallel to pressing. Such directional sintering may be attained by a two step pressing in which the sample is turned 90° prior to the second pressing. Another method may be liquid phase pressing resulting in random orientation of carbide particles.

Fabrication of NbC Billet - Flexural strength data for NbC appearing in the literature range from 35,600 psi<sup>10</sup> to 53,000 psi.<sup>11</sup> Extrapolation of the curve for strength as a function of carbide content for our materials suggests a value of 27,000 psi for pure NbC. In order to establish the NbC end point as related to the raw materials and fabrication process in use on our program, a billet of NbC was hot pressed at 2800°C/4000 psi/1 hr starting with stoichiometric amounts of niobium metal powder and calcined petroleum coke.

Sectioning of the finished billet showed that considerable grain growth had occurred toward the top of the billet. Microstructural examination of the upper and lower portions of the billet confirmed this grain size differential (Fig. 14). The dark phase in these micrographs are for the most part voids,



Upper Portion of Billet



Lower Portion of Billet

Fig. 14 - MICROSTRUCTURE OF NbC BILLET SHOWING DIFFERENCES  
IN GRAIN SIZE WITH RESPECT TO LOCATION  
(200X, etched)

and free carbon in these structures was extremely limited. The large grains toward the upper portion is probably due to grain growth in sintering. Density determinations revealed a range from 97.9% theoretical at the top to 93.3% at the bottom as shown in Fig. 15. From the observed grain growth and higher densities toward the top of the billet, it would appear that pressure during processing was greater at the top. Although the system is designed so that the sample is pressed from both ends, the pressure at the bottom may be distributed in part to the carbon black insulation under the bottom of the mold.

Strength determinations are also listed with respect to sample location in the billet. The detrimental effect of larger grain size on strength is apparent from these values. The relatively low value for sample 5C may be due to high porosity.

The strength data for NbC indicates that the aforementioned linear relationship between flexural strength and carbide content does hold for our particular raw materials and processing methods. A billet will be fabricated using NbC as the starting material to determine if any difference may exist if reaction sintering is not used.

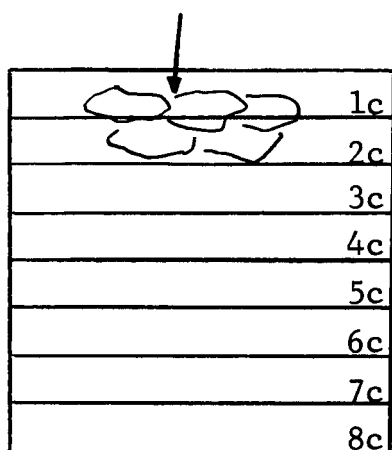
### III. CONCLUSIONS AND FUTURE WORK

During this period, processing studies were conducted to determine real vs indicated temperatures above 3000°C. Compositional studies have included HfC-C and ZrC-C composites as well as samples in the NbC-C and TaC-C systems. Properties studies have been involved with thermal expansion, flexural creep at 2400°C, and tensile strength measurements. The most significant findings in the present work are as follows:

- 1) Processing studies show that niobium metal in either powder or bulk (wire and foil) form reacts readily to form the carbide. At elevated temperatures (3200-3250°C) the carbide-carbon eutectic reaction is quite rapid. This is indicated by



Area of Grain Growth



1c
2c
3c
4c
5c
6c
7c
8c

Density  
% Theoretical

Flexural  
Strength, psi

97.9

19,770

97.8

20,190

97.5

29,580

96.6

94.7

22,590

93.5

93.4

93.3

Fig. 15 - DENSITY AND FLEXURAL STRENGTH VARIATIONS  
IN NbC BILLET

the ability of relatively large isolated volumes of carbide, i.e., a disc  $2\frac{1}{2}$ " diameter x  $\frac{1}{4}$ " high, to dissolve surrounding carbon and form the eutectic structure.

2) Compositional studies in the NbC-C system shows that at processing temperatures below 2900°C, composites of high density but poor bonding are obtained. This temperature appears to be a minimum for fabrication of high strength NbC-C bodies.

3) Material loss due to extrusion and reaction with the mold occurs in liquid state hot pressing of ZrC-C composites, even when the initial carbide content is dropped to 15 vol%. There appears to be a lower limit of 7-8% vol ZrC which is retained within the composite regardless of starting content, when ZrC-C bodies are processed at 3000°C.

4) Flexural creep studies at 2400°C/8000 psi/30 minutes show that susceptibility to creep in the NbC-C system increases with increasing carbide content. Under these conditions, TaC-C samples display creep resistance which is vastly superior to that of NbC-C.

5) Evaluation of A/G flexural strengths as a function of carbide content in both the TaC-C and NbC-C systems shows the relationship to be curvilinear. The relationship is linear for W/G data. These relationships can be explained on the basis of equating flexural stresses in the W/G direction to a parallel or constant strain model, and the stresses in the A/G direction to a series or constant stress model. The orientation of both the carbide and graphite phases are the basis on which these models become applicable.

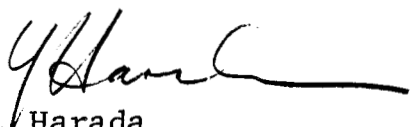
6) Evaluation of a pure NbC sample fabricated using our materials and techniques shows that the linear relationship between flexural strength and carbide content previously observed for various NbC-C compositions does hold at the NbC end point.

The apparatus for high temperature measurement of tensile and compressive strength has been modified and will be serviceable very shortly. The bulk of the work during the final quarter of this program will be devoted to obtaining property data at high temperatures.


IV. CONTRIBUTING PERSONNEL AND LOGBOOK RECORDS

In addition to the writer, the following personnel have been involved in this program: S. A. Bortz, R. Baker, and J. L. Sievert. Data are contained in Logbooks No. C17303, C17308, C17314, C17320 and C17323.

Respectfully submitted,  
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## REFERENCES

1. Harada, Y., "Graphite-Metal Composites," IIT Research Institute, Report No. IITRI G6003-F4, (July 28, 1965)
2. Harada, Y., "Graphite-Metal Composites," IIT Research Institute, IITRI Project G6003 Final Report, (Aug. 1, 1966)
3. Rudy, E., et al., "Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems," Aerojet-General Corporation, AFML-TR-65-2, Part I, Vol. V, (Jan. 1966).
4. Nadler, M. R. and Kempter, C. P., "Some Solidus Temperatures in Several Metal-Carbon Systems," J. Phys. Chem. 64(10)1468-71 (Oct. 1960)
5. Adelsberg, L. M., Cadoff, L. H. and Tobin, J. M., "Group IV B and V B Metal Carbide-Carbon Eutectic Temperatures," J. Am. Ceram. Soc. 49(10)573-74 (Oct. 1966).
6. Spriggs, R. M., et al., "Pressure-Sintered Nickel Oxide," Bull. Am. Ceram. Soc. 43(8) 572-77 (Aug. 1964)
7. White, J. L. and Pontelandofo, J. M., "Graphite-Carbide Materials Prepared by Hot Working," General Atomic, GA-6052, (Feb. 3, 1965)
8. Harada, Y., "Metal Carbide-Graphite Composites," IIT Research Institute, IITRI G6003-1, Quarterly Report No. 1 (Oct. 27, 1966)
9. Holliday, L., Composite Materials, Elsevier: Amsterdam, The Netherlands (1966) pp. 405-08
10. Shaffer, P.T.B., High Temperature Materials: No. 1, Materials Index, Plenum Press, New York (1964) p. 114
11. Merryman, R. G., Robertson, R. H. and Dietz, R. J., "Mechanical Properties: The Room Temperature Flexural Strength of Some Metal Carbide-Carbon Composites Hot Pressed by CMB-6," Los Alamos Scientific Laboratory, Report N-1-1824, (Oct. 25, 1966)